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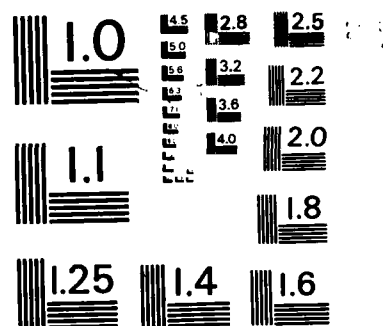
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The Reliability of Standard Rate Constants
For Rapid Electrochemical Reactions

by

Thomas Gennett and Michael J. Weaver

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Department of Chemistry

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THE RELIABILITY OF STANDARD RATE CONSTANTS
FOR RAPID ELECTROCHEMICAL REACTIONS

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Abstract

A method is outlined for testing the reliability of standard rate constants, k^S , for rapid electrode reactions evaluated using electrochemical perturbation techniques. This entails monitoring the response of the apparent *rate constants* values of k^S to systematic alterations of the double-layer structure caused by the addition of specifically adsorbed anions. These rate responses are compared with those observed at the same potential for structurally similar, yet irreversible, reactions for which reliable rate constant - potential data can be obtained using conventional d.c. methods. The procedure is applied to rate data obtained for Ru(III)/(II) ammine redox couples by comparing the measured rate increases resulting from the addition of *para*-toluenesulfonate anions with the corresponding rate increases seen for the irreversible reduction of Co(III) amines. Ruthenium(III)/(II) ammine couples, especially $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, are proposed as "reference reactions" with which to test the capabilities of different perturbation techniques for evaluating rapid standard rate constants and for intercomparing rate data obtained in different laboratories.



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Introduction and Background

Similarly to rate constants for self-exchange reactions in homogeneous solution, "standard" electrochemical rate constants k^s (i.e. those determined at the standard or formal potential E_f) are extremely sensitive to the chemical nature of the redox couple. At least at mercury electrodes it appears possible to obtain electrochemical rate constants, k_{el} , for simple outer-sphere processes with accuracies that approach those obtained for rates of redox reactions in homogeneous solution. This is most easily achieved for reactions having k_{el} at significant overpotentials in the range ca. 10^{-4} to 10^{-2} cm sec⁻¹. Under these circumstances the faradaic current can be accurately extracted from the background currents, and yet only small to moderate corrections for diffusion polarization and back reactions are typically required, even when using "slow perturbation" techniques such as d.c. polarography.¹ However, for redox couples that involve only small structural differences between the oxidized and reduced forms the standard rate constants approach, and possibly surpass, the range of values that are amenable to experimental evaluation, even using rapid perturbation techniques. Although the exact magnitude of this upper limit depends inevitably on the time scale of the particular technique and experimental conditions employed, it is commonly regarded as being in the range 0.5 - 5 cm sec⁻¹.¹ This limit arises from the vanishingly small contribution made by the electron-transfer kinetics to the overall cell response in relation to those provided by the solution resistance and from reactant diffusion to and from the surface. The evaluation of rate constants in this range is therefore subject to rapidly increasing uncertainties as k^s increases.

Values of k^S in the region ca $1 - 100 \text{ cm sec}^{-1}$ are typically predicted from contemporary electron-transfer theory for outer-sphere reactions involving small structural changes. [This follows from the anticipated preexponential factors $(10^4 - 10^5 \text{ cm sec}^{-1})^2$ combined with the activation free energy calculated for solvent reorganization (ca $3 - 6 \text{ kcal mol}^{-1}$)³]. Indeed, experimental values of k^S between ca $1 - 10 \text{ cm sec}^{-1}$ are commonly reported for such reactions.^{4,5} However, since such values are necessarily close to the upper limit for the particular technique employed, it is clearly important to ascertain in as unambiguous manner as possible the reliability of the measured rate constants. Despite the frequency with which such measurements are reported in the chemical literature, this question has seldom been considered. We present here a simple means by which the validity of such measurements can be checked for a given instrument, technique, and set of experimental conditions.

We have recently been evaluating standard rate constants for structurally simple one-electron redox couples involving inorganic and organometallic species in order to probe quantitatively the applicability of electron-transfer theories to outer-sphere electrochemical reactions.⁶ A particularly interesting group of reactants is provided by ruthenium(III)/(II) couples containing ammine, aquo, or related ligands. Both the Ru(III) and Ru(II) states are substitutionally inert, and the structural differences between them are small.^{7,8} Indeed such Ru(III)/(II) couples have been featured in several recent comparisons between experimental and theoretical rate parameters for outer-sphere electron transfer.^{6,8}

As with other multicharged reactants the observed values of k^S , k_{ob}^S , for the Ru(III)/(II) couples are sensitive to the double-layer composition. We have previously examined in detail the catalytic influence of specifically

adsorbed anions upon the outer-sphere electroreduction kinetics of several structurally similar Co(III) and Cr(III) complexes at mercury⁹⁻¹⁴ and solid metal surfaces.¹⁵⁻¹⁷ An important virtue of these reactants is that their substitution inertness prevents the occurrence of ligand-bridged pathways involving the adsorbed anions. By and large the double-layer effects are consistent with the simple Gouy-Chapman-Stern-Frumkin (GCSF) model⁹ once the likely noncoincidence of the reaction sites and the outer Helmholtz plane (o.H.p.) is taken into account.¹¹⁻¹⁴ Therefore we can write for one-electron reductions¹³

$$\log k_{ob}^E = \log k_{corr}^E - (F/2.303RT)(Z_r - \alpha_{corr})\phi_r \quad (1)$$

where k_{corr}^E is the double-layer corrected rate constant corresponding to k_{ob}^E at the same potential E (such as the standard potential), Z_r is the reactant charge number, α_{corr} is the double-layer corrected transfer coefficient, and ϕ_r is the average potential at the reaction site with respect to the bulk solution.

This simple predictable behavior suggested to us that a useful means of ascertaining the reliability of measured ("apparent") values of k_{ob}^S , $k_{ob}^S(\text{app})$, for reactions where the rate constants approach the anticipated upper limit of evaluation by a particular technique would be to examine the increases in $k_{ob}^S(\text{app})$ brought about by suitable alterations in double-layer structure. Sufficiently large negative changes in ϕ_r , $\Delta\phi_r$, can conveniently be induced by anion specific adsorption to yield large (ca $10 - 10^2$ fold) increases in k_{ob}^S . By selecting suitably strongly adsorbing anions large changes in ϕ_r can be induced by only small changes in the electrolyte composition, thereby maintaining the solution resistance (R_s) essentially constant. This strategy therefore provides a means by which the value of k_{ob}^S (i.e. the "charge-transfer" resistance R_{ct}) can be "tuned" over wide ranges while R_s

remains fixed. Consequently, values of $k_{ob}^S(\text{app})$ that vary with ϕ_r in the manner predicted by Eq. (1) indicate that they arise from R_{ct} as expected, so that $k_{ob}^S(\text{app}) \approx k_{ob}^S$. On the other hand, values of $k_{ob}^S(\text{app})$ that fail to respond to such variation in ϕ_r indicate that the true values of k_{ob}^S are beyond the range of the technique employed.

Two methods can be envisaged by which the values of $\Delta \log k_{ob}^S$ can be evaluated independently of the $k_{ob}^S(\text{app})$ measurements. Firstly, they can be estimated via Eq. (1) from the corresponding $\Delta \phi_r$ values determined from double-layer compositional data using the Gouy-Chapman model. While reasonable, this approach suffers from the limitations of Eq. (1) arising from the non-coincidence of the reaction site with the o.H.p. An alternative approach, employed here, involves the use of an electrochemically irreversible "calibration reaction" that features a redox couple of the same charge type and similar structure to the test reaction and yet exhibits sufficiently smaller rate constants so that their evaluation is entirely reliable. The latter approach eliminates the need for double-layer compositional data. Since on the basis of Eq. (1) the effect of altering the double-layer structure upon k_{ob}^S is determined by the reactant charge type and structure rather than by the absolute magnitude of k_{ob}^S , if the values of $k_{ob}^S(\text{app})$ are themselves reliable such increases in $k_{ob}^S(\text{app})$ should obey the approximate relation

$$\Delta \log k_{ob}^S(\text{app}) \approx \Delta \log (k_{ob}^{E^\circ})_{cal} \quad (2)$$

where $(k_{ob}^{E^\circ})_{cal}$ is the rate constant for the calibration reaction measured at the standard potential, E° , for the test redox couple. A marked breakdown in the applicability of Eq. (2), especially the observation that $\Delta \log k_{ob}^S(\text{app}) < \Delta \log (k_{ob}^{E^\circ})_{cal}$ above certain values of $k_{ob}^S(\text{app})$, would provide a clear indication that the limit of measurability of k_{ob}^S has been reached and that these values of $k_{ob}^S(\text{app})$ are untrustworthy.

The present report describes an illustrative application of this procedure to electrochemical rate data for $\text{Ru}(\text{NH}_3)_{6-x}(\text{OH}_2)_x^{3+/2+}$ couples, where $x = 0-2$, obtained at the mercury-aqueous interface using a.c. polarography. A crucial virtue of these systems is that the one-electron electroreduction kinetics of the corresponding $\text{Co}(\text{NH}_3)_{6-x}(\text{OH}_2)_x^{3+}$ complexes can be evaluated unambiguously in the vicinity of the Ru(III)/(II) formal potentials. (ca. -130 to -180 mV vs. the saturated calomel electrode, s.c.e.) by using d.c. or normal pulse polarography. Similar variations in k_{ob} at a given electrode potential, k_{ob}^E , are expected to be induced for corresponding Ru(III)/(II) and Co(III)/(II) couples by altering the double-layer structure on account of their identical charge, ligand composition, and similar electronic structure. By adding small ($\leq 1 \text{ mM}$) concentrations of *p*-toluene sulfonate (pTS^-) anions to the potassium hexafluorophosphate base electrolyte very large (up to ca 10^2 fold) increases in k_{ob}^E could be obtained for Co(III) reduction resulting from pTS^- adsorption. This provides a convenient means of altering k_{ob}^S for the Ru(III)/(II) couples from conveniently measurable values to those approaching the anticipated measurement limit and beyond. Comparison of the rate enhancements for Co(III) reduction with the increases in $k_{\text{ob}}^S(\text{app})$ observed for the corresponding Ru(III)/(II) couple therefore enables the reliability of the latter values to be critically assessed.

Experimental Section

$\text{Ru}(\text{NH}_3)_5\text{OH}_2 \cdot (\text{PF}_6)_3$ was prepared from air oxidation of $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$, synthesized as in ref. 18. $\text{Ru}(\text{NH}_3)_6 \cdot (\text{CF}_3\text{SO}_3)_3$ and $\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2 \cdot (\text{CF}_3\text{SO}_3)_3$ were gifts from Dr. G. M. Brown. The corresponding Co(III) complexes were synthesized as the solid PF_6^- salts using literature procedures:

$\text{Co}(\text{NH}_3)_6^{3+}$ ¹⁹, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ ²⁰, $\text{c-Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ ²¹. Sodium paratoluene-sulfonate (Aldrich Inc) and potassium hexafluorophosphate (Alfa Inorganics) were thrice recrystallized from water before use. Water was purified using a "Milli Q" system (Millipore Corp).

The electrochemical kinetic measurements employed a dropping mercury electrode with a mechanically controlled drop time of 2 secs. Reactant concentrations in the range 1 - 2 mM were generally employed. D.c. and normal pulse polarography was undertaken using a PAR 174A Polarographic Analyzer (E.C. & G. Instruments). Plots of the observed rate constants k_{ob} for the totally irreversible Co(III) reactions¹² against electrode potential E were obtained from such polarograms by using the analyses described by Oldham and Parry.²² The a.c. polarographic measurements employed a PAR 173/179 potentiostat, a PAR 175 potential programmer, and a PAR 5204 Lock-in amplifier. Frequencies between 100-1100 Hz with 10 mV. peak-to-peak amplitude were applied to the cell while the potential was swept at 1 mV sec^{-1} through the polarographic wave. The in-phase and quadrature components of the resulting impedance were plotted on a Houston 2000 X-Y recorder. The response of the instrument was deemed satisfactory for a.c. frequencies, ω , between 40-1400 Hz by measuring the ratio ($\cot \phi$) of in-phase to quadrature components for a Randles-type dummy cell as described in ref. 23. At frequencies above 2000 Hz the $\cot \phi - \omega^{1/2}$ plots exhibited significant deviations from the calculated curve for the dummy cell; this is probably due to response-time limitations of the potentiostat and current follower. Values of k_{ob}^{S} (app) were obtained from the slope of plots of $\cot \phi$ versus $\omega^{1/2}$ measured at the reversible "half-wave" potential for the redox couple, $E_{1/2}^{\text{r}}$, using²⁴

$$[\cot\phi]_{E_{1/2}} = 1 + (D_{\text{ox}}^{1-\alpha} D_{\text{red}}^{\alpha} / 2)^{1/2} [\omega^2 / k_{\text{ob}}^{\text{s}} (\text{app})] \quad (3)$$

where D_{ox} and D_{red} are the diffusion coefficients of the oxidized and reduced species, respectively, α is the observed cathodic transfer coefficient, and ω has the units radians sec^{-1} . Values of $E_{1/2}^{\text{r}}$ were obtained from polarography and cyclic voltammetry (the latter using a hanging mercury drop electrode); α was determined from

$$E_{\text{max}} = E_{1/2}^{\text{r}} + (RT/F) \ln[\alpha / (1-\alpha)] \quad (4)$$

where E_{max} corresponds to the maximum on the $\cot\phi$ - E plots at various a.c. frequencies.²⁴ Values of D_{ox} and D_{red} were obtained from the polarographic limiting currents for reduction and oxidation of the appropriate Ru(III) and Ru(II) species, respectively.

Most other experimental details are given in ref. 16. All potentials were measured against a saturated calomel electrode (s.c.e.), and all measurements were made at $23 \pm 0.5^\circ\text{C}$.

Results and Discussion

Figure 1 consists of the logarithm of the "apparent" rate constants, $\log k_{\text{ob}}^{\text{s}} (\text{app})$, observed using a.c. polarography for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in 0.1 M KPF_6 with progressively increasing concentrations of NapTS, plotted against the logarithm of the corresponding rate constants, $\log k_{\text{ob}}^{-175}$, for $\text{Co}(\text{NH}_3)_6^{3+}$ reduction at the formal potential for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ (-175 mV). *p*-Toluene-sulfonate was chosen as the adsorbing anion since it is noncomplexing yet sufficiently adsorbed at mercury, especially in the potential region of interest here, so that only very small bulk concentrations are required in order to yield large surface concentrations of adsorbed anions.^{9,25}

Thus ca. 50-fold increases in k_{ob} for $\text{Co}(\text{NH}_3)_6^{3+}$ reduction are induced by the addition of 1 mM NapTS at -175 mV (Fig. 1).

Although the values of k_{ob}^{-175} for $\text{Co}(\text{NH}_3)_6^{3+}$ reduction are very small (ca 4×10^{-6} cm sec $^{-1}$) in electrolytes containing little or no pTS $^-$, these rate constants as well as those at higher pTS $^-$ concentrations can nonetheless be obtained reliably by a short (≤ 100 mV) extrapolation of the linear log k_{ob} -E plots obtained from the totally irreversible d.c. polarograms. (These Tafel plots, extracted from currents on the rising portion of the polarographic wave, generally referred to values of k_{ob} between 10^{-4} and 10^{-2} cm sec $^{-1}$. The lower limit of k_{ob} is determined by the detection of current for Co(III) reduction in relation to the background currents, and the upper limit by the onset of complete diffusion polarization). That only minor changes in the bulk electrolyte composition are needed to yield large double-layer structural changes is an important virtue of this system. This minimizes the likelihood that changes in k_{ob}^s (app) for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ could be due in part to artifacts associated with alterations in R_s .

Potassium hexafluorophosphate was selected as the base electrolyte since PF_6^- anions are only weakly adsorbed in the potential region ca 0 to -400 mV, yielding only small positive values of the potential across the diffuse layer, ϕ_d , for concentrations in the range 0.1 - 0.5 M.^{13,26} The limited solubility of $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ in this medium necessitated the use of ionic strengths around 0.1 M. Values of k_{ob} obtained for the present reactions in 0.1 M KPF_6 should therefore be close to, yet significantly smaller than, the corresponding "double layer-corrected" rate constant, k_{corr}^{13} [Eq. (1)], provided that $\phi_d = \phi_r$. This latter assumption has been shown to be correct for Co(III) ammine reductions.^{12,13,16}

In view of Eq. (2), we expect that the plot in Fig. 1 should approximate a straight line with unit slope. (The line drawn through the point 1 has such a slope.) In actuality, the points 1-3 yield a reasonable straight line with a slope around 0.9, whereas at higher pTS^- concentrations (points 4-7 $[\text{pTS}^-] \geq 0.06 \text{ mM}$) progressively smaller increases in $\log k_{\text{ob}}^{\text{S}}(\text{app})$ are obtained relative to $\log k_{\text{ob}}^{-175}$. The last point in Fig. 1 (7), corresponding to $k_{\text{ob}}^{\text{S}}(\text{app}) \approx 2 \text{ cm sec}^{-1}$, represents the largest value of $k_{\text{ob}}^{\text{S}}(\text{app})$ that could meaningfully be evaluated from the $\cot\phi - \omega^{1/2}$ plots. Higher values of $k_{\text{ob}}^{\text{S}}(\text{app})$ yield plots with slopes that are statistically indistinguishable from zero within the range of a.c. frequencies employed, given the uncertainties in evaluating $\cot\phi$ from the a.c. polarograms.

Figure 2 shows the corresponding plot of $\log k_{\text{ob}}^{\text{S}}(\text{app})$ for the $\text{c-Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$ couple against $\log k_{\text{ob}}$ for $\text{c-Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ reduction, $\log k_{\text{ob}}^{-135}$, determined at the appropriate formal potential for this Ru(III)/(II) couple (-135 mV). Again, the straight line shown has a slope of 1.0. The points for the lowest pTS^- concentrations (1-5), corresponding to the smallest $k_{\text{ob}}^{\text{S}}(\text{app})$ and k_{ob}^{-135} values, yield an approximate straight line with slope ca 0.9, with the points corresponding to $k_{\text{ob}}^{\text{S}}(\text{app}) \geq 1.0 \text{ cm sec}^{-1}$ (6-10) deviating progressively further from this line. The reproducibility of the $\cot\phi - \omega^{1/2}$ plots, and hence $k_{\text{ob}}^{\text{S}}(\text{app})$, for $\text{c-Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$ was significantly greater than

those for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, at least for rate constants approaching the upper limit. This is because $\text{Ru}(\text{NH}_3)_6^{3+}$ slowly precipitated from solution, eventually yielding concentrations below the values (1-2 mM) desirable for accurate subtraction of the background currents. No such difficulties were encountered with $\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$ for which statistically nonzero $\cot\phi-\omega^{1/2}$ slopes could be obtained that correspond to values of $k_{\text{ob}}^{\text{S}}(\text{app})$ up to ca 4.5 cm sec^{-1} . Representative $\cot\phi-\omega^{1/2}$ plots for $\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$, corresponding to the data in Fig. 2, are shown in Fig. 3. The deviations from linearity seen for points 7-10 in Fig. 2 are considered to be outside the limits of experimental precision estimated on the basis of the observed scatter in the $\cot\phi-\omega^{1/2}$ plots (Fig 3).

The values of k_{ob} for $\text{c-Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ reduction in Fig. 2 (ca 5×10^{-3} to 0.5 cm sec^{-1}) are markedly larger than those for $\text{Co}(\text{NH}_3)_6^{3+}$ reduction in Fig. 1 (ca 5×10^{-6} to $2 \times 10^{-4} \text{ cm sec}^{-1}$). However, little systematic error is expected to be introduced into the evaluation of k_{ob} for either reaction due to the relatively short (100-200 mV) extrapolations of the Tafel lines involved together with the known reliability of d.c. polarography for accurately evaluating such plots.²⁷ In addition, the values of $\log k_{\text{ob}}^{\text{E}}$ obtained for both these reactions at a given electrode potential are very similar. Similar results to those in Figs. 1 and 2 were also obtained for $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$ by comparing the pTS^- rate accelerations with those seen for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ reduction at the same electrode potential (-162 mV).

These data therefore indicate that the values of $k_{ob}^s(\text{app})$ for both the Ru(III)/(II) couples determined using a.c. polarography approximate the corresponding "true" values, $k_{ob}^s(\text{true})$, for $k_{ob}^s(\text{app}) \lesssim 1.0 \text{ cm sec}^{-1}$, whereas $k_{ob}^s(\text{app}) < k_{ob}^s(\text{true})$ for $k_{ob}^s(\text{app}) \gtrsim 1.0 \text{ cm sec}^{-1}$, the magnitude of this discrepancy increasing rapidly as k_{ob}^s becomes larger. Admittedly, the slopes of the $\log k_{ob}^s(\text{app}) - \log k_{ob}^s$ plots are slightly smaller than that expected (1.0) even for $k_{ob}^s(\text{app}) < 1.0 \text{ cm sec}^{-1}$, suggesting that $k_{ob}^s(\text{app}) < k_{ob}^s(\text{true})$ even under these conditions. However, this is probably due to smaller changes in ϕ_d experienced by Ru(III)/(II) upon pTS^- adsorption in comparison with those for the corresponding Co(III)/(II) couple. This is expected in view of the slightly larger size of the ruthenium complexes placing the reaction site further from the electrode surface.¹¹ Therefore, on the basis of Figs. 1 and 2 the values of $k_{ob}^s(\text{app})$, at least in 0.1 M KPF_6 , appear to be close (at least within ca 50%) to the corresponding "true" standard rate constants, $k_{ob}^s(\text{true})$.

Support to this assertion is provided by examining the changes in $k_{ob}^s(\text{app})$ induced for $\text{Ru}(\text{NH}_3)_{6-x}(\text{OH}_2)_x^{3+/2+}$ couples by varying the number of aquo ligands x . Table I contains a summary of standard rate constants in 0.1 M KPF_6 for the three Ru(III)/(II) couples studied here, together with a value for $\text{Ru}(\text{OH}_2)_6^{3+/2+}$ determined previously in 0.2 M KPF_6 using cyclic voltammetry.²⁸ Since the values of ϕ_d^{GCS} in 0.1 M KPF_6 in this potential region are small and positive,¹³ the corresponding double layer-corrected rate constants, k_{corr}^s , obtained using Eq (1) are somewhat larger than k_{ob}^s (Table I; see footnotes for procedural details).

It is interesting to note that the substitution of aquo for ammine ligands leads to a progressive diminution in k_{corr}^s as well as in $k_{ob}^s(\text{app})$. Such decreases are indeed expected from structural considerations since it is known from x-ray crystallographic data that $\text{Ru}(\text{OH}_2)_6^{3+/2+}$ exhibits a

noticeably larger difference, Δa , in metal-ligand bond distance between the Ru(III) and Ru(II) forms (0.09 \AA)²⁹ than for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ (0.04 \AA).³⁰ These structural differences combined with metal-ligand force constants from vibrational spectroscopic data enable inner-shell reorganization energies to be obtained,⁷ which together with the theoretical estimates of the outer-shell (solvent) reorganization energy and the frequency factor² enable theoretical estimates of $k_{\text{corr}}^{\text{S}}$, $k_{\text{corr}}^{\text{S}}(\text{calc})$, to be obtained. By assuming that the same values of Δa also hold for the individual ruthenium-aquo and ruthenium-ammine bonds in the mixed-ligand complexes, values of $k_{\text{corr}}^{\text{S}}(\text{calc})$ can also be obtained for these systems. These values are also given in Table I. (See the footnotes for calculational details.³¹) Although the absolute estimates of $k_{\text{corr}}^{\text{S}}(\text{calc})$ are subject to some uncertainties given the assumptions involved,^{7,31} the relative values within such a reactant series should be quantitatively reliable.

Comparison of the corresponding values of $k_{\text{corr}}^{\text{S}}$ and $k_{\text{corr}}^{\text{S}}(\text{calc})$ in Table I shows that the observed decreases in $k_{\text{corr}}^{\text{S}}$ as the number of aquo ligands increases are very close to the theoretical expectations. Indeed, good agreement is also seen between individual values of $k_{\text{corr}}^{\text{S}}$ and $k_{\text{corr}}^{\text{S}}(\text{calc})$ for the three Ru(III)/(II) amines studied here. Since the values of k_{ob}^{S} for $\text{c-Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$ and $\text{Ru}(\text{OH}_2)_6^{3+/2+}$ are sufficiently small ($< 0.1 \text{ cm sec}^{-1}$) so to render their evaluation less susceptible to measurement errors, this finding further supports the reliability of the present $k_{\text{ob}}^{\text{S}}(\text{app})$ values obtained for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in 0.1 M KPF_6 .

It remains to consider possible reasons for the increasingly systematic deviations seen between the values of $k_{\text{ob}}^{\text{S}}(\text{app})$ at the highest pTS^- concentration in Figs 1 and 2 and the estimates of $k_{\text{ob}}^{\text{S}}(\text{true})$ obtained from the linear correlation plot. One obvious possibility is that the decreasing precision with which $k_{\text{ob}}^{\text{S}}(\text{app})$ can be obtained when the $\cot \phi - \omega^2$ slopes

become very small (Fig. 3) renders these deviations statistically insignificant. However, the error bars shown in Fig. 2, which were estimated from the $\cot\phi-\omega^2$ plots in Fig. 3, suggest that these discrepancies between corresponding values of $k_{ob}^S(\text{app})$ and $k_{ob}^S(\text{true})$ arise in part from nonrandom errors. One likely source of such error is associated with the presence of uncompensated cell resistance,³² even though positive feedback compensation was applied. Although higher a.c. frequencies could be used to attain higher values of $\cot\phi$, the commercial instrumentation used here displayed nonideal behavior under such conditions (*vide supra*).

Conclusions

The foregoing demonstrates the hitherto unexploited utility of the electrostatic double-layer effects exerted by specifically adsorbed anions upon suitable outer-sphere electrode reactions to provide a means for checking the reliability of standard rate constants obtained using a given perturbation technique. This approach can also be used to determine the practical upper limit to the standard rate constants that can be evaluated for a given set of experimental conditions using a particular technique.

The number of reactant systems that fulfill the criteria necessary for this approach is probably not large. However, the present Ru(III)/(II) redox couples offer a number of desirable features that prompt their utilization as "reference reactions" with which to test the relative merits of different techniques and to intercompare electrochemical rate data obtained in different laboratories. The $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couple is particularly suitable

for this purpose. Thus $\text{Ru}(\text{NH}_3)_6^{3+}$ may be obtained commercially in solid form which can easily be purified. Both the Ru(III) and Ru(II) forms are stable in aqueous solution over a wide range of pH values,³³ and in nonaqueous media.³⁴ The couple yields standard rate constants that can be varied from measurable values in KPF_6 electrolyte to values in other electrolytes whose evaluation should provide a stern test for even the most sophisticated rapid perturbation methods. Ru(III)/(II) couples could be utilized, for example, to provide objective tests of the assertion that there are "no electrode reactions with rate constants that lie beyond the reach of existing measurement methods".³⁵

A related redox couple, $\text{Ru}(\text{bpy})_3^{3+/2+}$ ($\text{bpy} = 2,2'$ -bipyridine) has also been proposed recently as a "reference reaction" for a similar purpose.³⁶ However $\text{Ru}(\text{bpy})_3^{3+/2+}$ has several serious drawbacks for such applications. These include its extremely positive standard potential which precludes the measurement of k^s on most electrode materials, including mercury, and its tendency to adsorb from aqueous media via the hydrophobic bipyridine ligands. In addition, values of $k_{\text{corr}}^s(\text{calc})$ are obtained for $\text{Ru}(\text{bpy})_3^{3+/2+}$ (ca. 100 cm sec^{-1})³¹ that are outside the range of existing measurement methods, so that the occurrence of unexpected and possibly artifactual experimental conditions are required to yield measurable values of k_{ob}^s for this couple. In contrast, the Ru(III)/(II) couples considered here have none of these disadvantages, and moreover offer formal potentials which lie in the range to enable k^s to be evaluated at a number of solid electrodes as well as at mercury.

It is hoped that these measurements of rapid rate constants for such reference reactions under systematically varying and well-defined double-layer conditions will encourage further efforts to obtain reliable values of k_{ob}^s and hence k_{corr}^s for a variety of redox couples. Such data are sorely

needed for the overdue development of a quantitative molecularly-based understanding of outer-sphere electrochemical reactivity.

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Table I. Standard Electrochemical Rate Parameters for Ru(III)/(II) Couples at the Mercury-Aqueous Interface; Comparison with Theoretical Predictions.

| Redox Couple | E_f^a mV. vs. s.c.e. | k_{ob}^s ^b | α^e | k_{corr}^{sf} | k_{corr}^s (calc) ^g |
|---|---------------------------|------------------------------|-----------------|-------------------------|----------------------------------|
| $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ | -175 | 0.35 | 0.65 ± 0.02 | 2.0 | 2.0 |
| $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$ | -162 | 0.25 | 0.64 ± 0.02 | 1.5 | 1.4 |
| $\text{c-Ru}(\text{NH}_3)_5(\text{OH}_2)_2^{3+/2+}$ | -135 | 0.17 | 0.61 ± 0.02 | 1.0 | 1.1 |
| $\text{Ru}(\text{OH}_2)_6^{3+/2+}$ | -20 | $\approx 5 \times 10^{-3}^d$ | --- | $\sim 5 \times 10^{-2}$ | 0.3 |

^a Formal potential of redox couple measured in 0.1 M KPF_6 .

^b Standard rate constant obtained in 0.1 M KPF_6 using a.c. polarography, except where noted.

^c 1 mM HClO_4 also present to suppress hydrolysis; quoted value is (0.85 x observed value) on basis of observed influence of 1 mM HClO_4 upon k_{ob}^s for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$.

^d Obtained in 0.2 M KPF_6 + 2 mM HPF_6 . Data from ref. 28.

^e Observed transfer coefficient in 0.1 M KPF_6 , determined from a.c. polarography using Eq. (3) (see text).

^f Double-layer corrected standard rate constant, determined from Eq (1) with $Z = 3$, $\alpha_{corr} \approx 0.5$. Values of ϕ_r at E_f for each redox couple estimated by extrapolation from data given in ref. 13. Taken as 18 mV for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$, 20 mV for $\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$ and $\text{Ru}(\text{OH}_2)_6^{3+/2+}$.

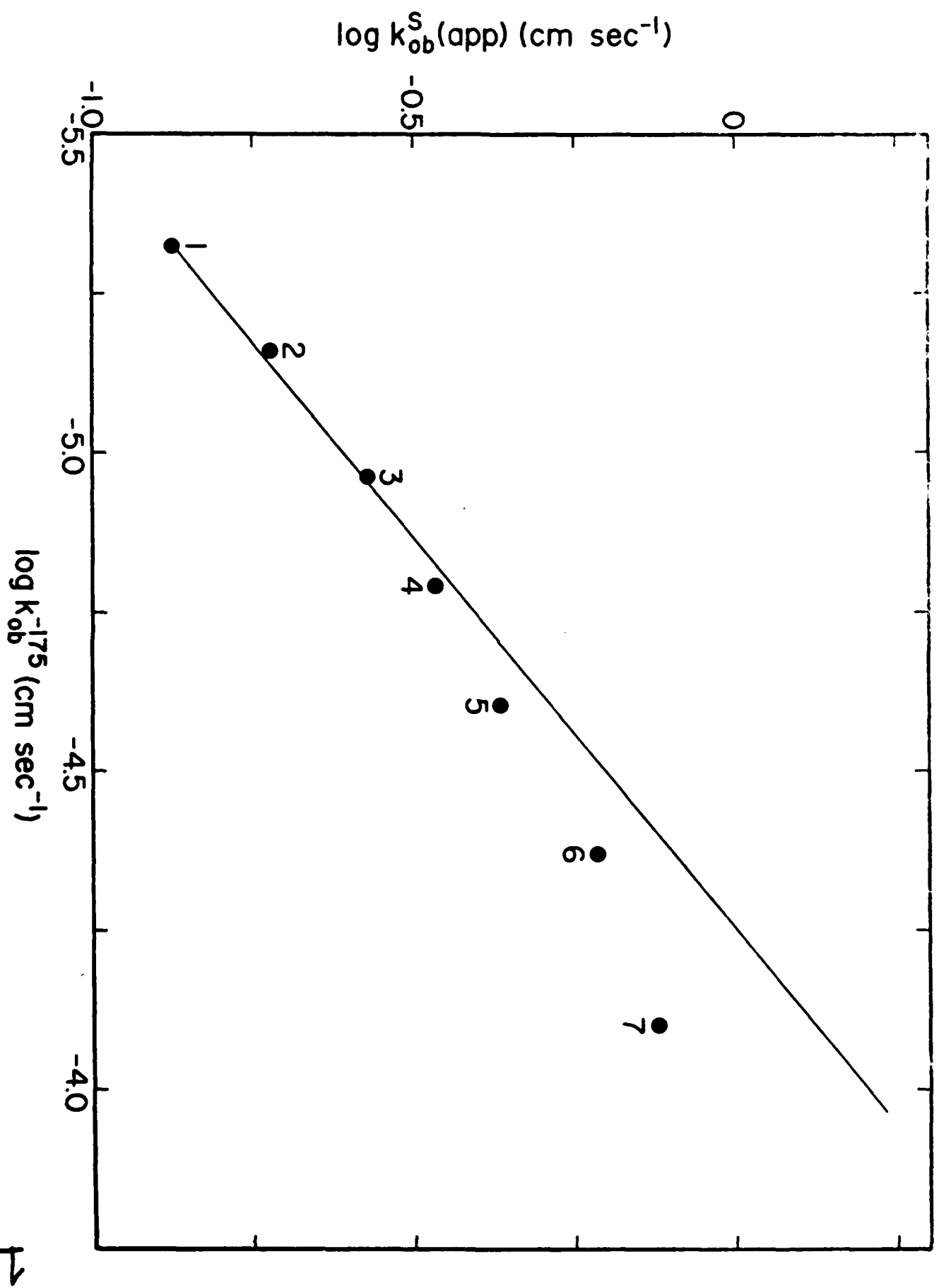
^g Standard rate constants calculated from outer-sphere electron-transfer theory, using^{2,8} $k_{calc}^s = \delta r v_n \exp[-(\Delta G_{is}^* + \Delta G_{os}^*)/RT]$, where δr is the "reaction zone thickness",² v_n is the nuclear frequency factor², and ΔG_{is}^* and ΔG_{os}^* are the activation free energies associated with inner- and outer-shell reorganization, respectively. These various quantities were taken or calculated as follows:^{6,31} $\delta r = 6 \times 10^{-8}$ cm.,² values of v_n from weighted mean of inner- and outer-shell rearrangement frequencies² [for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $v_n = 3.5 \times 10^{12}$ sec⁻¹, for $\text{Ru}(\text{OH}_2)_6^{3+/2+}$, $v_n = 7 \times 10^{12}$ sec⁻¹], inner-shell barrier from $\Delta G_{is}^* = 1/4 \sum_i (f_i \Delta a_i)^2$ (i.e. half the homogeneous inner-shell barrier), where f_i is the force constant of the i th metal-ligand vibration,⁸ and Δa is the difference in metal-ligand bond distances in the oxidized and reduced forms (0.09 and 0.04 Å for $\text{Ru}(\text{OH}_2)_6^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, respectively;^{29,30} outer-shell barrier ΔG_{os}^* from dielectric continuum model essentially as described in ref. 28. Further details will be available elsewhere.³¹

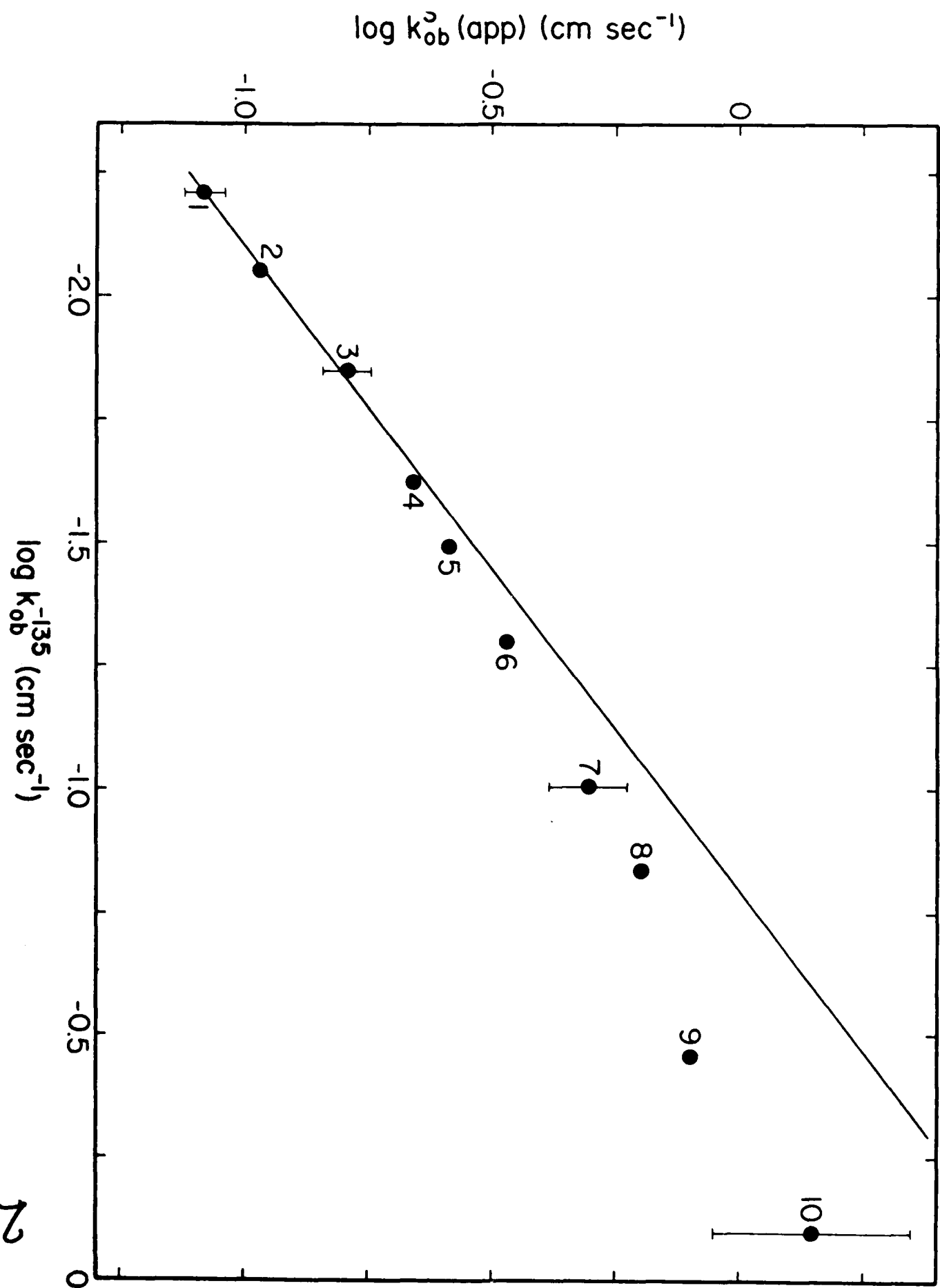
Figure Captions

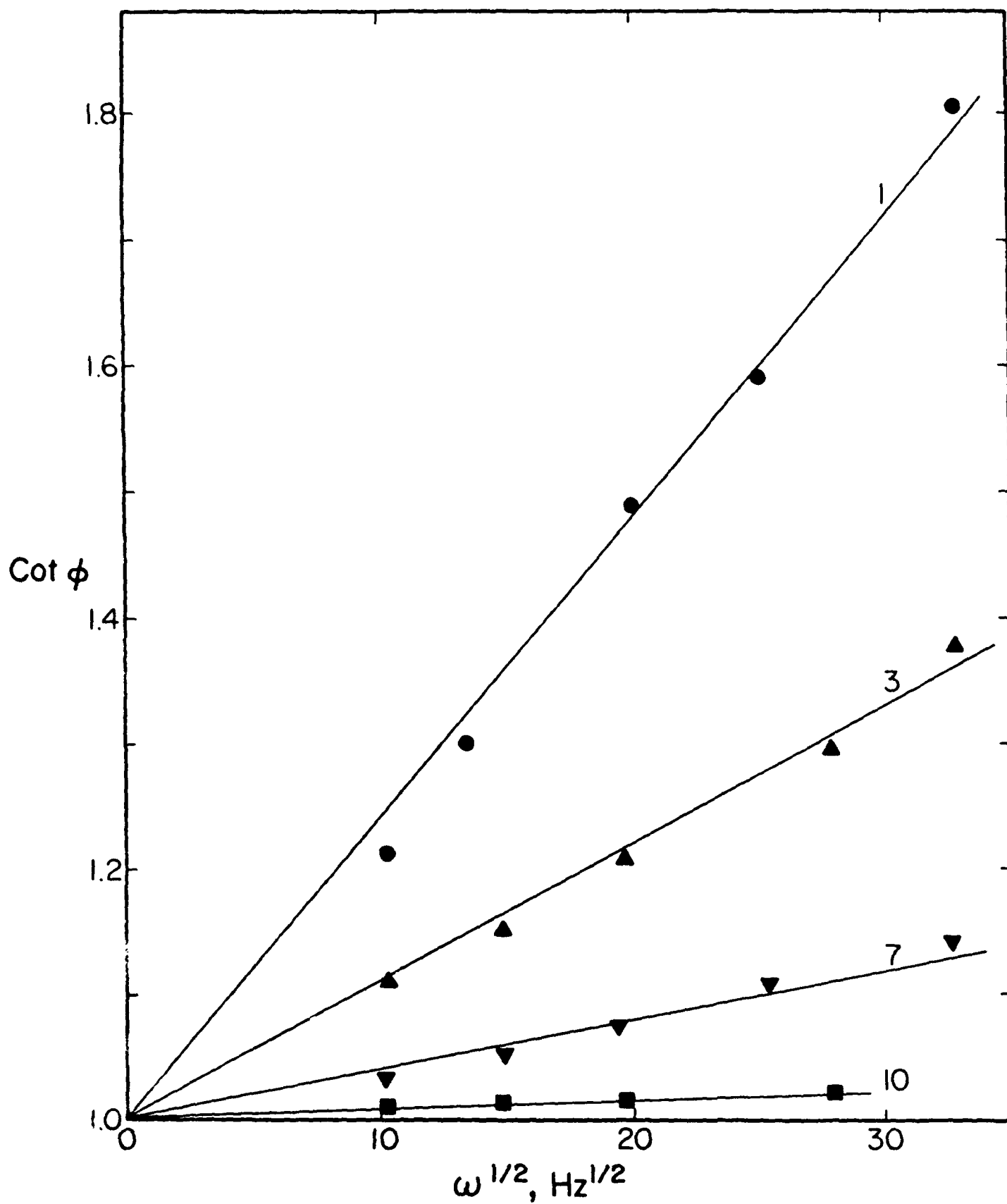
Figure 1. Plot of logarithm of observed standard rate constant (cm sec^{-1}) for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ measured using a.c. polarography, $\log k_{\text{ob}}^{\text{s}}(\text{app})$, in 0.1 M KPF_6 and for various additions of NapTS, against logarithm of observed rate constant for $\text{Co}(\text{NH}_3)_6^{3+}$ reduction, $\log k_{\text{ob}}^{-175}$, at same electrode potential (-175 mV) and in the same electrolytes. Key to NapTS concentrations: 1, 0mM; 2, 0.01; 3, 0.03; 4, 0.06; 5, 0.1; 6, 0.2; 7, 0.8mM. The straight line is drawn through point 1 and has a slope of 1.0.

Figure 2. Plot of logarithm of observed standard rate constant (cm sec^{-1}) for $\text{c-Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$ measured using a.c. polarography, $\log k_{\text{ob}}^{\text{s}}(\text{app})$, in 0.1 M KPF_6 + 1 mM HClO_4 and for various additions of NapTS, against logarithm of observed rate constant for $\text{c-Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ reduction, $\log k_{\text{ob}}^{-135}$, at same potential (-135 mV) and in the same electrolytes. Key to NapTS concentrations: 1 - 7, as in Fig. 1; 8, 1.6 mM; 9, 3.2 mM; 10, 10.8 mM. The straight line is drawn through point 1 and has a slope of 1.0.

Figure 3. Representative plots of $\cot\phi$ from a.c. polarograms for $\text{c-Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+/2+}$ at reversible half-wave potential (-135 mV) versus square root of applied frequency, $\omega^{1/2}$, in 0.1 M KPF_6 (line 1) and for three additions of NapTS (lines 3,7,10). Key to NapTS concentrations as in Fig. 2.







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